

A METHOD OF CONDITIONING IRON ALLOY-BASED ANODES  
FOR ALUMINIUM ELECTROWINNING CELLS

Field of the Invention

This invention relates to the conditioning of iron alloy based aluminium electrowinning anodes to form an integral electrochemically active iron-based oxide layer thereon, anodes so conditioned, aluminium electrowinning cells with such anodes and the production of aluminium in such cells.

Background Art

The technology for the production of aluminium by the electrolysis of alumina, dissolved in molten cryolite containing salts, at temperatures around 950°C is more than one hundred years old. This process and the cell design have not undergone any great change or improvement and carbonaceous materials are still used as electrodes and cell linings.

Using metal anodes in aluminium electrowinning cells would drastically improve the aluminium process by reducing pollution and the cost of aluminium production. Many patents have been filed on non-carbon anodes but none has found commercial acceptance, also because of economical reasons.

US Patents 4,614,569 (Duruz/Derivaz/Debely/Adorian), 4,680,094 (Duruz), 4,683,037 (Duruz) and 4,966,674 (Bannochie/Sherriff) describe non-carbon anodes for aluminium electrowinning coated with a protective coating of cerium oxyfluoride, formed in-situ in the cell or pre-applied, this coating being maintained by the addition of a cerium compound to the molten cryolite electrolyte. EP Patent application 0 306 100 (Nyguen/Lazouni/Doan), US Patents 5,069,771, 4,960,494 and 4,956,068 (all Nyguen/Lazouni/Doan) describe metallic anode substrates which may be further covered with such an in-situ formed protective cerium oxyfluoride layer.

US Patent 5,510,008 (Sekhar/Liu/Duruz) discloses an anode made from an inhomogeneous porous metallic body obtained by micropyrethically reacting a powder mixture of nickel, iron, aluminium and possibly copper and other elements. An electrochemically active oxide-based outer portion is formed by in-situ polarisation.

WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz) and WO01/42534 (de Nora/Duruz) disclose anodes produced from nickel-iron alloys which are surface oxidised to form a coherent and adherent outer iron oxide-based layer whose surface is electrochemically active surface.

WO01/42534 (Duruz/Nguyen/de Nora) discloses a nickel-iron alloy aluminium electrowinning anode with an openly porous electrochemically active surface produced by removal of iron from the surface, in particular by electrolytic dissolution of iron.

WO00/06805 (de Nora/Duruz) discloses an aluminium electrowinning anode having a metallic anode body which can be made of various alloys, for example a nickel-iron-copper alloy. The surface of the anode body is oxidised by anodically evolved oxygen to form an integral electrochemically active oxide-based surface layer. The oxidation rate of the anode body is equal to the rate of dissolution of the surface layer into the electrolyte. This oxidation rate is controlled by the thickness and permeability of the surface layer which limits the diffusion of anodically evolved oxygen to the anode body.

WO01/42536 (Duruz/Nguyen/de Nora) discloses an aluminium electrowinning anode made from a nickel-iron alloy having an openly porous outer portion which consists predominantly of nickel metal and which is obtainable by removal of iron from the alloy.

WO01/42534 (de Nora/Duruz), WO02/070785 (Nguyen/de Nora), WO02/083990 (de Nora/Nguyen), WO02/083991 (Nguyen/de Nora), WO03/014420 (Nguyen/Duruz/de Nora), WO03/078695 (Nguyen/de Nora) and WO03/087435 (Nguyen/de Nora) disclose further metal-based aluminium electrowinning anodes.

Metal or metal-based anodes are highly desirable in aluminium electrowinning cells instead of carbon-based anodes. Usually, the anodes are pre-oxidised in an oxidising atmosphere before use to produce an electrochemically active oxide layer thereon. In practice, prior to insertion into the cell, the metal-based anodes are usually pre-heated above the molten electrolyte to inhibit thermal shocks in the electrolyte and its solidification when the anode is immersed.

#### 10 Objects of the Invention

A major object of the invention is to provide a method of conditioning an iron-based alloy anode for aluminium electrowinning to increase its lifetime and improve its electrical conductivity during use.

15 Another object of the invention is to provide a method of conditioning an iron-based alloy anode to form an active anode surface that has a high electrochemical activity for the oxidation of oxygen ions for the formation of bimolecular gaseous oxygen and a low solubility in the electrolyte.

A further object of the invention is to provide a method of conditioning an iron-based alloy anode to form an integral electrochemically active oxide layer with an improved density and coherence and with limited ionic conductivity for oxygen ions and a low electrical resistance.

Yet another object of the invention is to provide a method of conditioning an aluminium electrowinning anode which is made of readily available alloys(s).

30 Yet a further object of the invention is to provide an aluminium electrowinning anode which is made of readily available alloys(s) and an aluminium electrowinning cell having such an anode.

#### Summary of the Invention

35 The invention is based on the observation that an integral oxide layer formed by oxidation of an iron-based

alloy, in particular an iron-based alloy comprising nickel and/or cobalt, is significantly denser and more coherent when the oxidation of the iron-based alloy is carried out by polarisation thereof in a molten electrolyte under  
5 specific conditions compared to oxide layers produced by conventional oxidation in air or by polarisation in a molten electrolyte as disclosed in the prior art.

To produce such a denser and more coherent oxide layer, the anode's active surface is up to immersion into  
10 the electrolyte essentially metallic and substantially unreacted with reactive species that form ceramic compounds with metals from the iron-based alloy. Such reactive species include oxygen at or above ambient temperature or fluorine-containing gases that could  
15 contact the anode while pre-heating the anode above the cell.

It has been found that the formation of such ceramic compounds on the iron-based alloy before polarisation in the electrolyte impairs the coherence and  
20 density of the oxide layer subsequently formed in-situ, which reduces its capacity to limit diffusion of oxygen and leads to thicker oxide layers with greater electrical resistance. It has been observed that this effect is most detrimental when the iron-based alloy is pre-oxidised  
25 before electrolysis and also when the iron-based alloy is pre-heated above the electrolyte in the fluorine-containing fumes prior to immersion into the electrolyte.

The invention relates to a method of conditioning a metallic anode structure for producing aluminium in a  
30 molten electrolyte containing dissolved alumina. The metallic anode structure has initially an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds, in particular oxides and fluorides, of metals from the  
35 metallic anode structure.

According to the invention, the method comprises the ordered steps of: (a) substantially preventing the essentially metallic active surface free of said ceramic compound from reacting with any reactable species, in

particular oxygen and fluorine species, until immersion into a molten electrolyte containing oxygen ions; (b) immersing into the molten electrolyte the metallic anode structure with its essentially metallic active surface free of said ceramic compounds; and (c) polarising the immersed metallic anode structure at a potential above the potential of oxidation of oxygen thereby evolving oxygen on the active anode surface and oxidising the active anode surface to form on the metallic anode structure a dense and coherent integral iron-based oxide layer which is electrochemically active for the oxidation of oxygen and which inhibits diffusion of oxygen towards the metallic anode structure.

The prevention of the metallic active surface from reacting with any reactable species, in particular oxygen and fluorine species, until immersion into a molten electrolyte can be achieved either by protecting the active surface against reaction, for instance by coating the surface with a temporary protective layer, or by avoiding exposure of the active surface to a reactive environment for an extended period of time during which a significant amount of anode constituents at the active surface can react with the environment.

For instance, exposure of a cast iron-based alloy to air at room temperature for a few days would not lead to significant formation of ceramic (oxide) compounds at its surface. However, when the iron-based alloy is cast and then left unprotected in the atmosphere for a long period of time before use, for example stored several months on a shelf after casting, the surface of the iron-based alloy can become noticeably altered which has been found to reduce the anode's performances, in particular the stability, lifetime and energy efficiency. Moreover, it has been discovered that even a short exposure, e.g. a few minutes, to fluorine-containing gases while pre-heating the anode above a fluoride-based molten electrolyte has a significant deleterious effect.

As opposed to the prior art anode conditioning methods in which the iron-based alloy anodes after casting were kept unprotected until immersion into the molten

electrolyte and also preferably were pre-oxidised in a high temperature oxidising atmosphere and/or pre-heated unprotected in fluorine-containing fumes above the molten electrolyte before immersion into the molten electrolyte, the method of conditioning the iron-based alloy anodes of the present invention prevents substantially any reactive interactions between the anode and the environment before immersion into the molten electrolyte.

In case, before use, the anode's alloy contains at its surface a noticeable amount of ceramic compounds produced by reaction of metals from the alloy's surface with a reactive environment, such ceramic compounds should be removed from the alloy's surface before carrying out the method of the invention.

Preferably, the method of the invention includes the step of pre-heating the metallic anode structure, prior to its immersion, to a temperature at which it can be immersed into the molten electrolyte without substantial solidification thereof. During this pre-heating step, the structure's essentially metallic active surface is maintained free of said ceramic compounds by substantially preventing the active anode surface from reacting with the environment during pre-heating before immersion. This is not the case with prior art methods, when the anodes are pre-heated without the inventive conditioning.

Protection of the active anode surface prior to immersion into the molten electrolyte can be achieved by covering the active surface with a temporary protective layer which is substantially impermeable to any species reactable with the active surface and which is removed prior to immersion into the molten electrolyte or dissolves therein as a fugitive coating.

When the anode is pre-heated in a reactive atmosphere prior to immersion, the temporary layer should be heat stable, for instance applied from a ceramic paint, e.g. an alumina-based paint, which is stable also at high temperature. Of course, a heat-stable protective coating

can be used even if the anode is not subjected to a pre-heat treatment.

When the anode structure is not pre-heated in a reactive atmosphere, the temporary layer for longlasting protection at ambient temperature before use, e.g. for storage, can be an organic paint or a substantially impervious wrapping, e.g. made of plastic.

The anode structure can also be pre-heated prior to immersion in an inert atmosphere that is substantially free from any species reactable with the active surface. In this case, no heat stable temporary protective layer is needed during the pre-heating.

The iron-based alloy outer part may comprise one or more elements selected from nickel, cobalt, copper, molybdenum, manganese, titanium, tantalum, tungsten, hafnium, vanadium, zirconium, niobium, chromium, cobalt, aluminium, silicon, carbon and the rare earth metals, in particular yttrium.

In one embodiment, the iron-based alloy outer part, consists essentially of: 45-55 weight% iron; 15-55 weight% in total of nickel and/or cobalt; 0-30 weight% copper; and 0-10 weight% in total of one or more further elements, usually selected from molybdenum, manganese, titanium, tantalum, tungsten, hafnium, vanadium, zirconium, niobium, chromium, cobalt, aluminium, silicon, carbon and the rare earth metals, in particular yttrium.

Further suitable iron-based alloy compositions for the anode structure are disclosed in WO00/40783 (de Nora/Duruz), WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz), WO01/42534 (de Nora/Duruz), WO01/42536 (Duruz/Nguyen/de Nora), WO02/014420 (Nguyen/Duruz/de Nora) and WO03/078695 (Nguyen/de Nora).

The metallic anode structure can be a cast alloy. Casting can be advantageously used to produce anodes of complex shapes, e.g. specially adapted for the circulation of electrolyte. Examples of such anode shapes are disclosed in WO99/02764 (de Nora/Duruz), WO00/40781, WO00/40782 and WO03/006716 (all de Nora).

The metallic anode structure can be quenched and/or annealed prior to immersion into the molten electrolyte, taking care however that the anode's active surface is not exposed to an environment that can substantially react with anode constituents at the active surface.

The invention also relates to a method of conditioning or reconditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina, for example when the metallic anode structure has been impaired by exposure to a reactive environment before use or when the anode structure has been worn during use.

Such a used or impaired metallic anode structure comprises an iron-based alloy outer part having a surface which is covered with ceramic compounds, in particular oxides and fluorides, of metals from the outer part. The conditioning or reconditioning method comprises the steps of: removing substantially all ceramic compounds from the surface of the outer part to form an essentially metallic active anode surface; and then conditioning as described above the metallic anode structure with its essentially metallic active anode surface free of any ceramic compounds.

A further aspect of the invention relates to method of electrowinning aluminium. This method comprises the steps of: conditioning a metallic anode structure as described above including polarising it in a molten electrolyte to form on the anode structure a dense and coherent integral iron-based oxide layer; and electrolysing dissolved alumina in the same or a different molten electrolyte using the conditioned anode structure to evolve oxygen thereon and produce aluminium on a facing cathode.

The dense and coherent integral iron-based oxide layer of the anode structure can be further formed during electrolysis by slow oxidation of the metallic anode structure at the metallic structure/oxide layer interface. Constituents of the dense and coherent integral iron-based



oxide layer at the oxide layer/electrolyte interface may slowly dissolve into the electrolyte during electrolysis, preferably at a rate corresponding to the oxidation rate of the metallic anode structure at the metallic structure/oxide layer interface, as disclosed in  
5 WO00/06805 (de Nora/Duruz).

As disclosed in WO00/06802 (Duruz/de Nora/Crottaz) the aluminium production molten electrolyte can comprise an amount of dissolved iron species and dissolved alumina  
10 sufficient to inhibit significantly dissolution of constituents of the dense and coherent integral iron-based oxide layer at the oxide layer/electrolyte interface.

The anode can be protected against the electrolyte with a cerium oxyfluoride-based outermost coating deposited  
15 and/or maintained during use, for example as disclosed in the abovementioned US Patents 4,614,569, 4,680,094, 4,683,037 and 4,966,674.

Preferably, the aluminium production molten electrolyte is maintained at a temperature below 960°C,  
20 preferably between 840°C and 940°C.

The aluminium production molten electrolyte can contain NaF and AlF<sub>3</sub> in a molar ratio in the range from 1.2 to 2.4. The alumina content in the aluminium production molten electrolyte is usually below 10 weight%, typically  
25 between 5 weight% and 8 weight%.

It is preferred that alumina-depleted electrolyte is circulated away from the electrochemically active iron-based oxide layer, enriched with alumina, and alumina-enriched electrolyte is circulated towards the  
30 electrochemically active iron-based oxide layer. Such an electrolyte circulation can be achieved by following the teachings of WO99/41429 (de Nora/Duruz), WO99/41430 (Duruz/Bellò), WO00/40781, WO00/40782, WO01/31088 and WO03/006716 (all de Nora).

35 Another aspect of the invention relates to an aluminium electrowinning anode structure. This structure comprises an iron-based alloy metallic outer part covered with a dense and coherent integral iron-based oxide layer

obtainable by conditioning by the above described method a metallic anode structure having an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds of metals from the metallic anode structure.

Compared to pre-oxidised anodes or anodes that are pre-heated unprotected in fumes above the molten electrolyte, the anode of the invention exhibits upon use in an aluminium electrowinning cell a more protective denser and more coherent oxide layer which is thinner and more conductive, as demonstrated in the example.

The invention also relates to an aluminium electrowinning anode structure having an iron-based alloy metallic outer part with an active anode surface. Before use, the active surface is essentially metallic and free of any ceramic compounds of metals from the metallic anode structure and is covered with a temporary protection medium. This protective medium substantially prevents ceramic-forming reactions at the essentially metallic anode surface and is separable from the active surface prior to immersion into the molten electrolyte or by contact with the molten electrolyte. Usually, the temporary protection medium is removable prior to immersion into the electrolyte or soluble in the electrolyte.

The temporary protection medium may comprises one or more substantially impervious solid layers. Suitable layers comprise at least one of ceramics, such as alumina, including ceramics applied from colloids, for instance colloidal alumina precursor, such as Nyacol™ and/or Condea™, and other colloid precursors of ceramics; metals, in particular reactable metals, such as aluminium, iron, copper, chromium or yttrium, for reacting with possibly diffusing reactive gases; polymers, e.g. plastic, in particular wrapping the anode structure under vacuum or inert gas or carrying one or more of the above layer constituents. Furthermore, the temporary protection medium can comprise an inert liquid or viscous material, such as oil or grease, or an inert gas, such as nitrogen or carbon

dioxide, for example within a polymer enclosure or wrapping around the anode structure.

The protective layer can comprise alumina, in particular applied from a paint or slurry, and/or a polymer. The protective layer may also contain metallic particles that trap a possible oxygen diffusion before it reaches the metallic anode surface.

Yet another aspect of the invention relates to an aluminium electrowinning cell comprising at least one oxygen-evolving anode structure as described above.

Preferably, the cell comprises an aluminium-wettable cathode preferably having an aluminium-wettable coating, in particular a drained cathode. Suitable, aluminium-wettable coatings are disclosed in US Patent 5,651,874 (de Nora/Sekhar), and PCT publications WO98/17842 (Sekhar/Duruz/Liu), WO01/42168 (de Nora/Duruz) and WO01/42531 (Nguyen/Duruz/de Nora). Suitable drained cathode designs are disclosed in US Patents 5,683,559, 5,888,360, 6,093,304 (all de Nora), 6,258,246 (Duruz/de Nora), as well as PCT publications WO99/02764 (de Nora/Duruz), WO99/41429 (de Nora/Duruz), WO00/63463 (de Nora), WO01/31086 (de Nora/Duruz) and WO01/31088 (de Nora).

#### Detailed Description

The invention will be further described in the following Examples:

#### Comparative Example

##### Conditioning:

A prior art-type conditioning of an anode was carried out as follows.

An anode was made by pre-oxidising in air at 1100°C for 3 hour a substrate of a cast nickel-iron alloy consisting of 50 weight% nickel, 0.3 weight% manganese, 0.5 weight% aluminium, 0.05 weight% C and 49.15 weight% iron, to form a very thin oxide surface layer on the alloy.

The surface-oxidised anode was cut perpendicularly to the anode operative surface and the resulting section of the anode was subjected to microscopic examination.

5 The anode before use had an outer portion that comprised an electrolyte-pervious, electrochemically active iron-rich nickel-iron oxide surface layer having a thickness of up to 10-20 micron and, underneath, an iron-depleted nickel-iron alloy having a thickness of about 10-15 micron containing generally round cavities filled with  
10 iron-rich nickel-iron oxide inclusions and having a diameter of about 2 to 5 micron. The nickel-iron alloy of the outer portion contained about 75 weight% nickel.

Underneath the outer portion, the nickel-iron alloy had remained substantially unchanged.

15 Testing:

An anode prepared as above was pre-heated unprotected in electrolyte fumes above an aluminium electrowinning cell for 20 minutes and then tested therein.

20 The cell contained a molten electrolyte at 880-890°C consisting essentially of NaF and  $\text{AlF}_3$  in a weight ratio NaF/ $\text{AlF}_3$  of about 0.7 to 0.8, i.e. an excess of  $\text{AlF}_3$  in addition to cryolite of about 24 weight% of the electrolyte, and approximately 5 weight% alumina. The  
25 alumina concentration was maintained at a substantially constant level throughout the test by adding alumina at a rate adjusted to compensate the cathodic aluminium reduction. The test was run at a current density of about 0.8 A/cm<sup>2</sup>, and the electrical potential of the anode  
30 remained in the range of 4.2 to 4.5 volts throughout the test.

During electrolysis aluminium was cathodically produced while oxygen was anodically evolved which was derived from the dissolved alumina present near the  
35 anodes.

After 24 hours, electrolysis was interrupted and the anode was extracted from the cell. The external

dimensions of the anode had remained substantially unchanged during the test and the anode showed no signs of damage.

5 The anode was cut perpendicularly to the anode operative surface and the resulting section of the used anode was subjected to microscopic examination.

It was observed that the anode was covered with an iron oxide surface layer having a thickness of 100 to 120 micron and consisting essentially of  $\text{Fe}_2\text{O}_3$  with less than 5  
10 weight% nickel oxide.

#### Example 1

An anode was made of the same metals as in the comparative Example except that it had an active surface essentially metallic and free of any ceramic compounds, in  
15 particular neither oxides nor fluorides, of metals from the anode's surface.

The cold anode was immersed in the molten electrolyte of a cell without prior reaction of the anode's active surface with a reactive environment, i.e.  
20 with the active surface essentially metallic and free of said ceramic compounds.

The molten electrolyte was at a temperature of 880-890°C and consisted essentially of NaF and  $\text{AlF}_3$  in a weight ratio NaF/ $\text{AlF}_3$  of about 0.7 to 0.8, i.e. an excess  
25 of  $\text{AlF}_3$  in addition to cryolite of about 24 weight% of the electrolyte, and approximately 5 weight% alumina.

Upon immersion of the anode, the electrolyte froze around the anode which prevented electrolysis. After 10 to 15 minutes in the electrolyte, the temperature of the  
30 anode had reached the melting point of the electrolyte and the electrolyte contacting the anode had molten thereby permitting electrolysis.

During the test, the alumina concentration was maintained at a substantially constant level throughout  
35 the test by adding alumina at a rate adjusted to compensate the cathodic aluminium reduction. The test was

run at a current density of about 0.8 A/cm<sup>2</sup>, and the electrical potential of the anode remained in the range of 4.0-4.3 volts throughout the test, i.e. about 0.2 V lower in average than in the above comparative test with a pre-oxidised and fume pre-heated anode.

During electrolysis aluminium was cathodically produced while oxygen was anodically evolved which was derived from the dissolved alumina present near the anodes.

After 24 hours, electrolysis was interrupted and the anode was extracted from the cell. The external dimensions of the anode had remained substantially unchanged during the test and the anode showed no signs of damage.

The anode was cut perpendicularly to the anode operative surface and the resulting section of the used anode was subjected to microscopic examination.

It was observed that the anode was covered with an iron oxide surface layer having a thickness of about 100 micron and consisting essentially of Fe<sub>2</sub>O<sub>3</sub> with less than 5 weight% nickel oxide and additionally an outermost layer of oxides of iron and aluminium having a thickness of about 25 micron.

The iron oxide surface layer, with pores of 3 to 5 micron, was denser than the oxide layer of the above comparative anode that had pores of 5 to 10 micron. This greater density of the oxide layer of the anode conditioned according to the invention provides a better protection for the alloy located underneath oxidation and electrolyte attack.

#### Example 2

Example 1 was repeated with a pre-heating step of the anode above the molten electrolyte prior to immersion into the electrolyte.

To prevent reaction of the essentially metallic anode surface with electrolyte fumes, the anode was

covered with a protective layer of alumina applied from an alumina-based colloidal slurry.

5 The colloidal slurry comprised an alumina colloid carrier consisting essentially of water and colloidal alumina particles in an amount of 20 weight% of the colloid, for example Nyacol™, and suspended alumina particles in an amount of 60 weight% of the colloidal slurry.

10 The anode was dipped into the slurry and allowed to dry to produce an alumina coating having a thickness of 0.6 to 1.0 mm covering and protecting the essentially metallic anode surface against reaction with the environment.

15 After pre-heating the protected anode for about 1 hour in the electrolyte fumes above the molten electrolyte, the anode was immersed with its alumina coating into the molten electrolyte. The protective alumina coating was dissolved almost instantaneously and normal electrolysis could start.

20 During electrolysis, the anode behaved like the anode in Example 2. After 24 hours, the anode was removed and examined. The anode upon use was not significantly different to the anode of Example 2.

25 In a variation, the protective effect of the alumina slurry can be improved by substituting half of the suspended alumina particles with suspended metallic particles, such as aluminium, iron and/or copper particles, which trap a possible oxygen diffusion before it reaches the metallic anode surface. Thus, in case the  
30 temporary protective coating is not perfectly impervious to the environment, reactive constituents of the environment will react with the metallic particles of the coating and substantially not with the metallic active anode surface.